PERFORMANCE OF THE LOW TEMPERATURE FIRST STAGE OF HRI'S CATALYTIC TWO-STAGE LIQUEFACTION PROCESS

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ABSTRACT

Hydrocarbon Research, Inc. (HRI), under the sponsorship of the U. S. Department of Energy (DOE), is developing a catalytic two-stage coal liquefaction process. The process consists of two direct-coupled ebullated-bed reactors in series, with the first stage operated at lower temperatures (<800°F) than typically used in direct liquefaction. Studies of both bituminous and sub-bituminous coals in a nominal 50 lb/day continuous, integrated recycle bench unit have shown considerable improvements in both distillate yield and product quality over other processes. In order to better understand the chemistry of the unique first-stage reactor conditions, a special on-line sampling system was added to the bench unit. Samples obtained over a wide range of operating conditions indicate that the first stage is an efficient hydrogenation system, achieving balanced rates of coal conversion and dissolution, solvent to coal hydrogen transfer, solvent regeneration, and liquefaction product upgrading and stabilization. Differences in responses of the two coals studied are noted and discussed.

INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has long been actively involved in the development of coal liquefaction process technology. The H-Coal® Process, featuring a single-stage ebullated-bed catalytic reactor, was successfully developed and demonstrated through operation of a 200 ton per day pilot plant at Catlettsburg, Kentucky, in the early 1980's.(1) In 1981-1982, HRI conducted a series of laboratory investigations to evaluate various two-stage liquefaction concepts which featured a thermal first-stage reactor followed by a closely coupled, ebullated bed, catalytic second stage.(2-6) The results of these programs formed the basis for the current Catalytic Two-Stage Liquefaction (CTSL) concept, which features two direct-coupled, ebullated-bed reactors in series. Under DOE sponsorship, HRI has been conducting a development program for the CTSL Process since 1983. Program results have been reported(7-11) with C_4-975°F distillate yields of 65 W % MAF coal achieved for both Illinois No. 6 and Wyodak coals. The process economics have been shown to be favorable in comparison with other two-stage approaches by an independent contractor's study(12) for both coals.

PROCESS FEATURES

The salient features of the CTSL Process are listed in Table 1. The key feature which distinguishes this from other single- or two-stage processes is the operation of a low temperature (<800°F) first-stage liquefaction reactor which contains an effective hydrogenation catalyst. Here, coal is converted by dissolution in the recycle solvent at a controlled rate, allowing the catalytic hydrogenation reactions important for solvent regeneration and liquefaction product stabilization to keep pace with the rate of coal conversion. The second stage, operating at conditions more similar to the single stage H-Coal® Process (but still less severe), finishes the job of coal conversion while converting primary liquefaction products to high quality distillates. Overall, the process produces higher yields of better quality distillate products than competing technologies.

It is generally recognized that coal conversion to liquids is a thermal process (involving hydrogen transfer from donor compounds in the recycle solvent), and that the function of a catalyst in a direct liquefaction system is to hydrogenate the solvent to provide those donor compounds, as well as to upgrade the thermal liquefaction products. As a result, two-stage liquefaction concepts were developed which featured a thermal first-stage liquefaction reactor, followed by a catalytic second stage for solvent hydrogenation and product upgrading. These are represented by the Integrated Two Stage Liquefaction (ITSL) processes developed at Lummus-Crest[13] and the Wilsonville Advanced Coal Liquefaction Pilot Plant,[14] and the Direct Coupled Two-Stage Liquefaction system (DC-TSL) developed at HRI. These processes rely on production of a high quality recycle donor solvent, produced at low (<800°F) catalytic stage temperatures which favor hydrogenation over cracking. One primary drawback to this sequential approach is that solvent donor compounds are depleted in the non-catalytic liquefaction reactor, so that the final "spent" solvent quality is much poorer than the inlet recycle solvent. Also, the lack of catalytic product stabilization leads to undesirable regressive recombination reactions at the conditions necessary to achieve complete coal conversion.

The CTSL Process avoids these drawbacks by conducting liquefaction at a much slower rate in the low-temperature first stage. The first stage conditions provide a very efficient hydrogenation atmosphere so that hydrogen shuttling compounds in the solvent can be effectively regenerated and reused over and over again. Thus the solvent does not become "spent". Primary liquefaction products are also efficiently hydrogenated as they are formed, reducing the tendency for regressive reactions. By conducting conversion and hydrogenation functions simultaneously rather than sequentially, the "lifetime" of unstable thermal products is reduced. The second stage then completes the coal conversion at more typical liquefaction temperatures in the presence of a much higher relative concentration of high quality solvent. Second-stage conditions are chosen to optimize coal and residuum conversion and heteroatom removal, without approaching a thermal severity where dehydrogenation of first-stage products become significant. This paper presents data to support each of the first-stage functions listed in Table 1, which in turn provide the basis for the observed overall performance benefits of the two-stage concept.

BENCH UNIT DESCRIPTION

Process development studies have been conducted in HRI's continuous two-stage Bench Unit 227, shown in Figure 1. It is necessary to study the process in a continuous unit with self-sustained recycle solvent generation in order to fully understand the results and avoid the pitfalls of smaller batch or once-through experimental units. The unit features two 2000cc ebullated-bed reactors in series. A special high-pressure, on-line sampling system was adapted to the first-stage reactor to obtain the data required to independently assess the effectiveness of the two reactor stages. Prior to this, it was necessary to attempt to interpret the effects of first-stage variables based on overall results only. Since the reactors are direct-coupled, and the desired sample quantities represent a significant fraction of the first-stage reactor inventory, the design and operation of the sampling system is critical to obtain representative samples while minimizing unit disruption. The data presented in this paper are based on analyses of the first-stage samples. A continuous atmospheric still was also added to the unit during this program to provide accurate control of recycle solvent cut points. The atmospheric still bottoms are subjected to further batch filtration and/or vacuum distillation operations to study various recycle oil preparation techniques. System inventories are minimized in order to provide a rapid lineout response to condition changes.

PROGRAM HISTORY

A summary of bench unit operations conducted through February 1986 is shown in Table 2. The first year of the program was dedicated to Illinois No. 6 coal, and the second year to Wyodak sub-bituminous coal. Following renewal of the contract for two additional years in 1985, additional studies are being conducted with Illinois No. 6 coal. Each of these coals has been studied in previous single- and two-stage operations, so that an extensive data base for comparison of CTSL results exists. The implementation of the first-stage sampling system, late in the original Illinois coal program, greatly enhanced the understanding of the observed favorable performance, and first-stage sample analyses were used extensively in all subsequent work.

FIRST-STAGE PERFORMANCE

Coal Conversion Rate

One of the primary benefits of the lower temperature liquefaction stage is that coal is converted at a controlled rate, allowing a balance between thermal and catalytic reaction rates to be maintained. Figures 2 and 3 show the relationship between coal conversion (to quinoline solubles) and both temperature and residence time for several sets of data for both coals. In each case, the connected data points represent studies where all other parameters (second-stage conditions, solvent/coal ratio, etc.) are held constant. Comparisons of non-connected points should not be made since other parameters are different as well. Note that increasing severity by both parameters always results in an increased coal conversion, indicating kinetic rate control. It should also be noted that overall process conversions were in all cases substantially higher, and tended to correlate with first-stage conversions. In the case of the Illinois No. 6 coal, it appears that "maximum" coal conversions (95-96%, typically) are being approached at 750-775°F, while the Wyodak coal is much slower to convert and requires additional thermal severity (90-93% conversion typically achieved in second stage).

Hydrogen Transfer Efficiency

Figure 4 shows the atomic hydrogen/carbon ratio of THF insoluble IOM from both first- and second-stage samples as a function of coal conversion for Wyodak coal. Surprisingly, this ratio stays quite high (at or above the original coal level) over a wide range of first-stage conversions. It would be expected that the most reactive components of the coal would be the most hydrogen-rich, and would leave behind a residue of depleted hydrogen content. This in fact does occur in higher temperature, thermal processes. However, the controlled conversion rate in CTSL allows for efficient hydrogen transfer to the coal as it reacts. A similar relationship has been noted for the Illinois No. 6 coal. Only at the more severe thermal conditions of the second stage does the hydrogen transfer appear to drop off, as evidenced by the lower H/C ratios for the high conversion samples.

No attempt has been made here to distinguish "unreacted coal" from IOM formed by regressive reaction. However, the combination of the observed kinetic response, residue analyses, and mild severity conditions indicate that regressive reaction should be minimal in the first stage. While residue analyses are interesting, they are of limited utility, particularly since the overall coal conversions achieved in CTSL are no better than in the single-stage H-Coal® Process. Of more importance are the analyses of the liquids which are formed at first-stage conditions, which are substantially different than those produced in other direct liquefaction processes.

Solvent Hydrogentation

Since the coal is liquefied in the presence of a catalyst at conditions which favor hydrogenation, donor species present in the solvent can be regeneratively rehydrogenated. This is illustrated for a typical condition for each coal in Table 3, which compares properties of first-stage oil and pressure filter liquid (PFL), which is both the second-stage oil and process recycle solvent. Note that even though substantial coal conversion has occurred in the first stage in each case, there is no indication of solvent quality deterioration - in fact, the solvent quality, as measured by standard microautoclave tests, has improved. This is due to simultaneous solvent hydrogenation, as indicated by the improved hydrogen content and lower aromatics level in the first-stage liquid. This is a key difference from other two-stage processes, where solvent quality is depleted in the liquefaction stage due to more severe thermal conditions and the lack of an effective hydrogenation catalyst. One positive benefit of this effect on the overall process is that the feed solvent/coal ratio can be set at a minimum pumpable level, without concern for available donor hydrogen levels. Bench unit operations on Illinois No. 6 coal have been conducted at feed slurry solvent/coal ratios as low as 1.1, and still lower ratios may well be possible on a larger scale. This has a large favorable impact on process economics.

Recycle Residuum Hydrogenation

Residuum in the recycle solvent is upgraded by hydrogenation in the first stage, making it more reactive for cracking to lighter distillates in the second stage. This is indicated in Table 4, which shows net positive yields of residuum components in the first stage, and net conversion to distillates in the second stage. As a result, the overall 975°F+ yields are quite low, and the quality (as indicated by high oil and low preasphaltene contents) is also quite good.

Catalytic Stabilization/Upgrading of Primary Liquefaction Products

The discussion above had highlighted the effect of first-stage conditions on recycle solvent properties. In fact, the oil properties presented are for liquids which are a blend of recycle solvent and direct first-stage products. Depending on feed solvent/coal ratio and net first-stage reactions, the first-stage oil content is estimated to be 20-50% directly produced from coal, with the remainder derived from recycle solvent. (Of course, in an integrated operation all of the material is ultimately coal-derived; here the distinction is being made to specifically include material which has not yet been exposed to second-stage conditions.) With this in mind, the level of hydrogenation is even more notable since the primary liquefaction products should be of substantially lower quality than the recycle solvent.

COAL COMPARISON

Evidence has been presented for both Illinois No. 6 and Wyodak coals which support the process concept of first-stage hydrogenation, resulting in improved overall liquid yields and product qualities. However, the response of the two coals - and hence the optimum process conditions for each - are quite different. As has been noted in Figure 2, the sub-bituminous coal is much slower to convert, and probably requires a first-stage temperature of at least 750°F to achieve enough coal conversion for the catalytic treatment to be effective. The bituminous coal liquefies much more readily, but (as noted in Table 4) gives much higher net residuum yields. Work to date has indicated optimum performance at 750-775°F, but it is probable that this can be reduced by the appropriate combination of catalyst, space velocity, etc. This objective is being pursued in the present program. Other items being investigated include optimization of liquid yield distribution, particularly the extinction conversion of all 650°F+ products, and operation at lower second-stage temperatures to improve product quality and extend catalyst life.

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TABLE 1

HRI'S CATALYTIC TWO STAGE LIQUEFACTION PROCESS

FIRST STAGE

"Low" Temperature (<800°F)
Hydrogenation Catalyst (e.g. Amocat 1C, NiMo)

Functions: Coal Conversion (controlled rate)
Hydrogen Transfer to Reacting Coal
Solvent Hydrogenation - Regenerative
Recycle Residuum Hydrogenation
Catalytic Stabilization/Upgrading of Primary Liquefaction Products

SECOND STAGE

"High" Temperature (>800°F)
Hydroconversion Catalyst (e.g. Amocat 1A, CoMo)

Functions: Complete Coal Conversion (Thermal in an improved solvent environment)
Residuum Conversion to Distillate Products
Heteroatom Removal
Avoid Dehydrogenation

OTHER PROCESS FEATURES

Reaction Stages are Direct-Coupled
Ebullated Bed Technology Scaleable Based on H-Coal®/H-Oil® Experience
Highest Conversion to Distillates of any Direct Liquefaction Process
More Aliphatic/Petroleum-Like Products than other Direct Liquefaction Processes

FIGURE 1

EBULLATED-BED BENCH UNIT 227

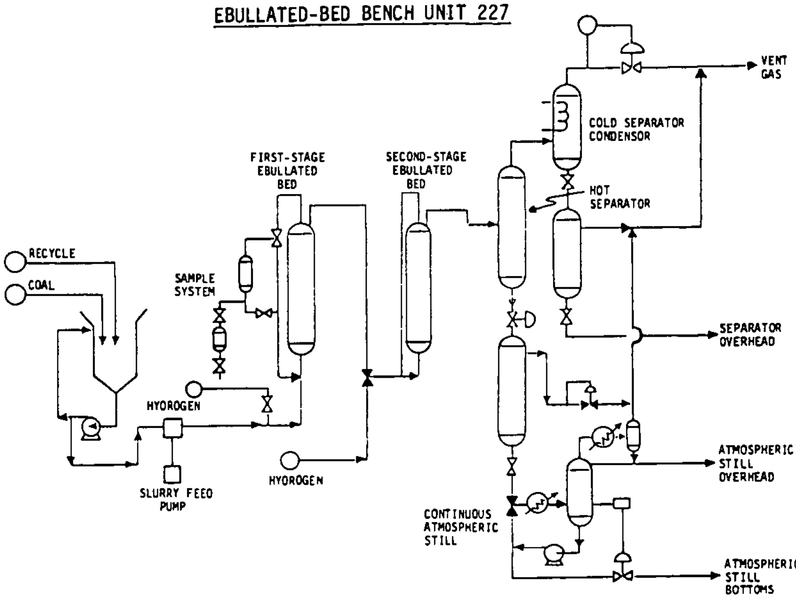


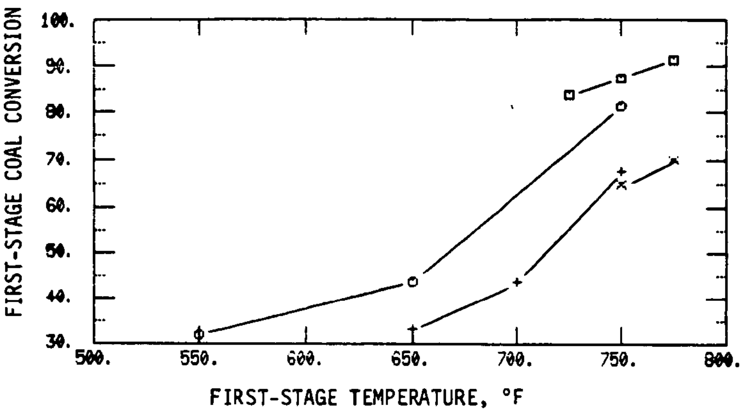
TABLE 2

CATALYTIC TWO STAGE LIQUEFACTION PROCESS DEVELOPMENT
History of Bench Unit Operations (through February 1986)

	Number of Runs	Number of Days	Conditions	First Stage Samples
Illinois No. 6 Coal (1983-1984)				
Process Variable Studies	8	149	38	-
First Stage Sampling	1	12	4	4
Process Demonstration	1	25	1	-
Total Illinois No. 6 (1983-1984)	10	186	43	4
Wyodak Sub-bituminous Coal (1983-1985)				
Process Variable Studies	3	80	25	18
Process Demonstration	2	44	3	8
Total Wyodak Coal	5	124	28	26
Illinois No. 6 Coal (1985-1986)				
Process Variable Studies	2	57	16	15

FIGURE 2

FIRST-STAGE COAL CONVERSION (W % MAF)
VERSUS TEMPERATURE



o Illinois No. 6 (Run 227-18)
□ Illinois No. 6 (Run 227-32)
+ Wyodak, Run 227-22 (Conditions 4, 5 and 6)
x Wyodak, Run 227-22 (Conditions 7 and 9)

FIGURE 3

FIRST-STAGE COAL CONVERSION (W % MAF) VERSUS TIME

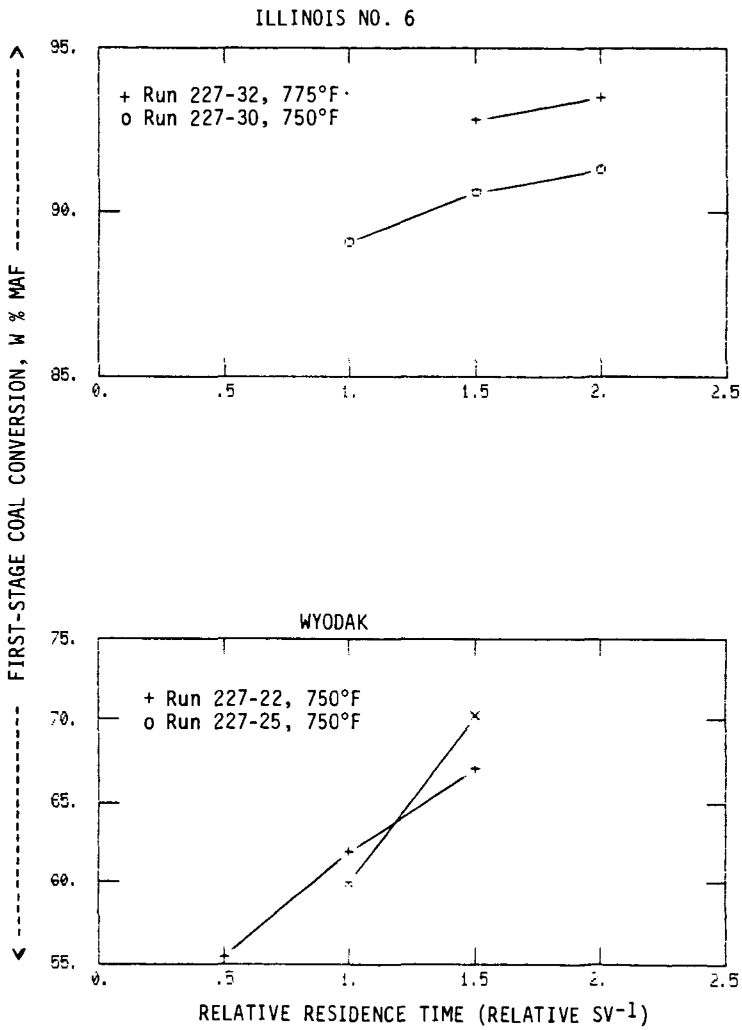
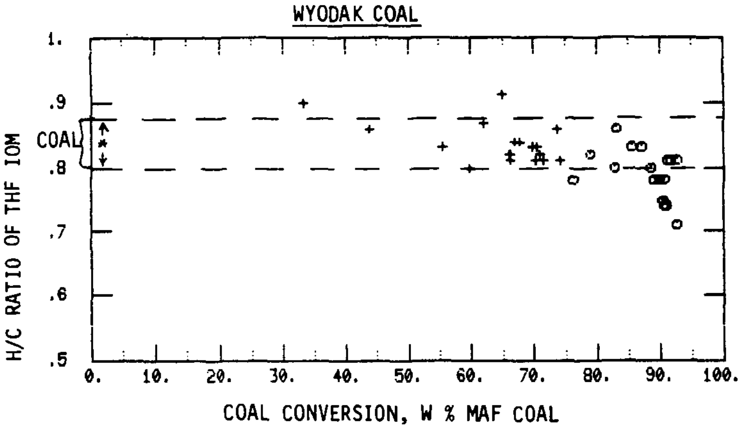


FIGURE 4

REACTOR SOLIDS HYDROGEN/CARBON ATOMIC RATIO VERSUS COAL CONVERSION



+ First-Stage Solids
o Second-Stage Solids
* Range of Analyses for Fresh Coal

TABLE 3

COMPARISON OF FIRST-STAGE OIL AND PFL PROPERTIES

	ILLINOIS NO. 6 COAL Run No. 227-18-12		WYODAK COAL Run No. 227-25-16	
	< ----------- S T A G E S ----------- >			
	FIRST OIL	SECOND PFL	FIRST OIL	SECOND PFL
Bench Unit Coal Conversion, W % MAF	87.1	92.7	73.6	91.6
Microautoclave Solvent Quality Test, W % THF Conversion				
HRI(1)	83.3	76.6	54.5	52.0
Conoco(2)*	82.9	79.9	64.5	64.0
H/C Ratio - 650-850°F	1.28	1.25	1.40	1.40
850-975°F	1.19	1.13	1.34	1.24
975°F+	0.95	0.91	1.06	0.98
Proton* NMR - % Aromatics				
850°F- Distillate	14.6	15.7	11.0	10.6
850°F+ Residuum	29.2	31.4	19.3	25.3

(1) HRI procedure uses matched coal and solvent.
(2) Conoco procedure uses Indiana V coal.
* *Data provided by CONOCO.*

TABLE 4

975°F+ RESIDUUM PROPERTIES

	ILLINOIS NO. 6 Run 227-32-9		WYODAK Run 227-25-16	
	< ------- S T A G E S ------- >			
	First	Second	First	Second
W % 975°F+ In Oil	39.5	32.1	12.1	9.0
975°F+ Properties				
H/C Ratio	1.03	0.99	1.06	0.98
% Nitrogen	0.65	0.53	0.79	0.73
% Oil	64.5	71.9	75.3	84.7
% Asphaltenes	28.6	23.5	24.1	15.0
% Preasphaltenes	6.9	4.6	0.6	0.3
Estimated Net 975°F+ Yield - W % MAF Coal				
Oils	9.6	-3.2	2.4	-0.2
Asphaltenes	9.3	-7.2	2.2	-1.8
Pre-Asphaltenes	3.3	-2.9	0.1	-0.1
TOTAL	22.2	-13.3	4.7	-2.1